

PATENT SPECIFICATION (11)

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(54) METHOD AND APPARATUS FOR THE DISCONTINUOUS SAMPLING AND PROPORTIONING OF GASES, VAPOURS, OR MIXTURES THEREOF

(71) We, AKADEMIE DER WISSENSCHAFTEN DER DDR, of 5, Rudower Chaussee, 1199 Berlin, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method and an apparatus for the discontinuous taking of samples from gases, vapours, or mixtures thereof at temperatures above their dew point from product flows, reaction chambers, or vessels and for introducing these samples in the form of gas, vapour, or mixtures of gas and vapour into analysis apparatus, particularly into gas chromatography columns.

Methods and apparatus for sampling and proportioning gases and vapours are known. For this purpose elastic closure caps or disks provided on reaction tubes, pipes, or vessels are generally perforated by a cannula and part of the material to be sampled is sucked up with the aid of a piston which is slidable gas-tightly in a tube connected to the cannula.

For analytical examination a sample of this kind is then introduced into the carrier gas current of a gas chromatography column.

The proportioning syringe is the most usual form of sampling and proportioning device. A special form, which is particularly suitable for taking and proportioning gas samples containing readily condensable fractions is equipped with a suitable heating jacket. Other proportioning syringes are equipped with a valve on the cannula attachment, so that the sample drawn into them can be stored for some time before being introduced into the gas chromatography

column. In addition, a proportioning syringe is known which at the end of the cylinder remote from the cannula attachment has a lateral aperture through which the material sampled flows when the piston is drawn back, thus flushing out the cannula and cylinder.

Known proportioning syringes have the disadvantage that individual components of the material sampled accumulate through sorption on the wall during flushing and filling, thus altering the composition of the proportioned sample. Furthermore, it is a disadvantage that when introduced into the gas chromatography column the sample is compressed in the cannula and proportioning syringe. Particularly in the case of mixtures in gas and vapour form there may thus be uncontrollable condensation of individual components, and the original composition of the sample is altered. Moreover, part of the sample remains in the dead space of sampling and proportioning devices of this kind, and thus is not available for analytical examination.

In addition, methods and apparatus are known in which the material sampled, in gas and/or vapour form, is passed through a pipe or a bore serving as proportioning chamber. This proportioning chamber is then separated from the current of sampled material by means of valves, slide valves, or a multiway cock. The sample taken is then introduced for analysis purposes into the separating column of a gas chromatography apparatus with the aid of a current of carrier gas. In special models the proportioning chamber or the entire apparatus may be cooled or heated. Methods of this kind, generally known as loop proportioning, have the disadvantage that relatively large volumes of material to be sampled are required in comparison with the amount to be metered,

because the proportioning chamber must first be thoroughly flushed out with the material which is to be sampled. For this purpose the proportioning device, which is located on or in the gas chromatography apparatus, is usually connected by a pipe to the sampling point, or a large volume sample vessel is filled with material at the sampling point and taken to the gas chromatography apparatus, where the sample is passed through the proportioning chamber into the analysis apparatus with the aid of a pressure gradient. The use of a sample vessel of this kind entails the additional disadvantage that in the sampling of gases containing vapour fractions their composition is altered by sorption effects or partial condensation.

Sampling methods and apparatus similar to loop proportioning are also known, in which sorbents or carrier materials impregnated with liquid, or else flow resisting means inert in relation to the material being sampled, are disposed in the proportioning chamber. When a gas-vapour phase is passed through an apparatus of this kind, the proportioning chamber optionally being cooled, condensable, sorbable, or soluble components are accumulated, and thus the composition of the material being sampled is considerably changed even during the taking of the sample. The sample is generally metered into the analysis apparatus by allowing the carrier gas to flow by way of the heated proportioning chamber into the separating column of the gas chromatography apparatus.

In another customary method material to be sampled, which consists of a mixture of gas and vapour having a dew point above room temperature, is separated by condensation into a gas fraction and a liquid fraction, and the two fractions are analysed separately. The gas contains fractions of the components which have predominantly accumulated in the condensate, while fractions of the components of the gas are dissolved in the condensate. During transport to the analysis apparatus or during the storage of the samples before they are introduced into the analysis apparatus an irreversible modification of the gas sample frequently occurs, for example by sorption, or of the liquid sample, for example by degasification, so that some fractions of the sample escape analysis. The errors in the individual analyses of the gas fraction and liquid fraction and also the error in the determination of the quantitative ratio of the gas and liquid fractions make it impossible to obtain adequately accurate analyses of gas-vapour mixtures having a dew point above room temperature.

The invention seeks to provide a rational method, which can be repeated as often as desired at short intervals of time, and also an instrument suitable for carrying out this method, which method and instrument will permit the accurate taking and proportioning of samples in gas and/or vapour form from corresponding

media in an amount such as is actually necessary for analytical examination, preferably by gas chromatography, for which purpose neither pipes nor large volume sample vessels are necessary for the transport of the sampled material, while at the same time avoiding irreversible variation of the composition of the sample by enrichment or impoverishment resulting from a sorption or condensation effect until the sample is introduced, either immediately or after a storage period, into the analysis apparatus.

The problem underlying the invention is therefore that of developing a method and an apparatus for the discontinuous sampling of gases, vapours or mixtures thereof at temperatures above their dew point from product flows, reaction chambers, or vessels and for introducing these samples in the form of gas, vapour or mixtures of gas and vapour into analysis apparatus, particularly into gas chromatography apparatus.

According to the invention this problem is solved in that an amount suitable for subsequent analysis - namely a volume of between 0.001 and 5 ml, but preferably between 0.01 and 0.5 ml - of the material in gas and/or vapour form that is to be analysed is drawn in or introduced into a tube which is provided with closure devices at both ends, by a sampling probe, while the sampling probe, the closure devices and the tube - or at least the sampling probe and the tube closure device which is connected thereto - are at a temperature above dew point of the material samples, and while during the drawing-in or introduction of the sampled material into the tube by the sampling probe no fraction of the sampled material shall reach the opposite end of the tube which is dimensioned in length according to the required volume of the sampled material; then the closure devices are closed, the sampling probe is removed from the material being sampled, the sampling column - consisting of the tube, closure devices and sampling probe - is connected either immediately or after its storage to the analysis apparatus, and the sample contained in the sampling column is introduced into the analysis apparatus by way of a gastight connection and with the aid of a gas current after the closure devices have been opened. It is preferable for the closure devices of the sampling column to be opened only after the sampling probe has been immersed into the material from which a sample is to be taken and optionally after the sampling probe has been flushed out with that material. The sample is advantageously taken by drawing off from the sampling column a volume of gas corresponding to the volume of the sample by way of the closure device of the sampling column situated downstream in relation to the direction in which the material being sampled flows in. Before the sample is introduced into the analysis apparatus, residues of sampled material are

analysis apparatus. If, for the purpose of feeding the sample into a gas chromatography column, the flow of the carrier gas is opposite to the direction in which the material flows in during the taking of the sample, the sample will be introduced into the separating column without any noticeable deterioration of separating power.

It is preferable for the tube of the sampling column of the invention to be made of stainless steel and to have an inside diameter between 0.1 mm and 10 mm, preferably between 0.2 mm and 6 mm, and a length conforming with the required volume of the sampled material, i.e. a tube length which is generally such that the free internal volume of the tube is from 2 to 5 times as great as the sample volume to be metered into the analysis apparatus, to ensure that when an amount of sampled material suitable for subsequent analysis is sucked in no part of it will reach the rear end of the tube of the sampling column. With an inside diameter of 2 mm, for example, a tube length of about 300 mm has been found satisfactory. The tube of the sampling column is optionally filled with granular material or with a sorption agent, in order in particular to increase the volumetric capacity of the apparatus of the invention, since fractions of the sample are reversibly absorbed by these filling materials. The capillary inside diameter or the granular filling of the tube of the sampling column ensure a uniform flow when the sampled material is being sucked in.

The novel sliding valves have in particular given excellent results as closure devices for the apparatus of the invention. However, other closure devices, such as cocks or needle valves, are also suitable provided that they enable the sample to be transferred without loss from the tube of the sampling column to the analysis apparatus in a brief metering operation. The sliding valve has a closure element consisting of a steel capillary tube having an outside diameter for example of 1.5 mm and an inside diameter of 0.3 mm, which tube is guided inside a stuffing box, preferably of polytetrafluoroethylene, and inside a metallic pressure bush.

Since the indentation provided in the closure element and lying near the tube of the sampling column is situated outside the stuffing box, which for example is of polytetrafluoroethylene, both when the slide valve is in the open position and when it is in the closed position, it is made impossible for the sealing material which is under pressure to flow into the indentation of the closure element. The indentation is carefully rounded. Its shape ensures that when the indentation passes through the stuffing box no polytetrafluoroethylene is torn off. In addition, the indentation can receive small amounts of abraded material formed in the course of dozens of operating cycles, without the closure element becoming clogged.

If, as in the preferred embodiment, the closure element of the slide valve merges into the sampling probe, a spring steel wire pressed into the capillary bore of the tip of the sampling probe reliably prevents material from being punched out when inserted into the self-sealing insertion disk at the sampling point, whereby the capillary probe would be clogged, but on the contrary the material sampled can pass unhindered through the lateral indentation into the sampling probe. The stuffing box of elastic, freely slidable material, preferably polytetrafluoroethylene, is resiliently chambered by the screwthreads of the pressure bush and by the pressure bush itself, which is subject to the action of a spring washer, in order to compensate for the different coefficients of expansion of metal and sealing material. The adjustment of the pressure bush is fixed by means of a lock-nut. The screwthreads of the pressure bush receive a stop the position of which is fixed by the end of the bore in the screwthreads when the valve is open, and by a cap nut when the valve is closed. The bores in the pressure bush and in the cap nut ensure double guidance. Outside the valve body the stop carries a handle and then tapers to a conical connector (1/10) which serves for connection to the analysis apparatus. Since the closure element is soldered to the stop only at the conical connector which forms one end of the guide sleeve, the closure element is resiliently centred by the pressure bush in every position.

For the successful application of the method of the invention it is essential that the materials of the apparatus should be inert in relation to the gas and/or vapour mixture which is to be analysed. Any separation, diffusion, and/or absorption processes which may possibly occur in the sampling column are made reversible by the apparatus of the invention and by the above described method of transferring the sample to the analysis apparatus. The invention permits the unfalsified taking of instantaneous samples from gases, vapours, or mixtures thereof, above their dew point, from product flows, reaction chambers, or vessels in an amount suitable for subsequent analysis, and enables them to be introduced in the form of gas, vapour, or mixtures of gas and vapour into analysis apparatus, preferably gas chromatography apparatus.

Variations of a product flow or of a reaction mixture may take place at short intervals of time (≥ 2 seconds), since the material sampled can be drawn off in rapid succession and if desired analysed only after a convenient storage period. This is the case if the time required for analysis exceeds the interval of time between successive samplings. Furthermore, it is an advantage that with closure devices - particularly slide valves - closed the sample can be stored for a number of hours in the sampling column and, if desired, can be transported to analysis equipment installed at a distance. Tests have

flushed out of the sampling probe while the closure devices are closed. It is expedient for the sample to be introduced from the sampling column into the analysis apparatus oppositely to the direction in which the sampled material flows in during the taking of the sample by the sampling probe. Immediately before and during the introduction of the sample into the analysis apparatus the sample is, if necessary, heated to a temperature above its dew point. For the heating of the sample a low voltage is applied direct to the sampling column.

For the application of the method use is made of an apparatus comprising a sampling column consisting of a tube having an inside diameter between 0.1 and 10 mm, preferably between 0.2 and 6 mm, which at both ends carries gastightly closing closure devices having no dead spaces, and which at one end is also provided with a sampling probe, while suitable connectors for gastight connection are provided on both closure devices. The interior of the tube of the sampling column may optionally be filled with a sorption agent or with a granular material, the granular material being fixed at both ends of the tube by a wire fabric screen. For the purpose of heating the sample it is preferable for the tube of the sampling column to form the heating resistor of a low-voltage heating system. Slide valves, whose closure element consists of a tube having a capillary bore which is closed in the closure element from one end as far as a lateral indentation which frees the capillary bore, have been found particularly suitable as gastightly closing closure devices having no dead spaces. The length of the closed part in the closure element (that is to say the part thereof not having the capillary bore) corresponds to the distance by which the closure element can be displaced in its longitudinal direction between two stop surfaces for the purpose of opening and closing the slide valve. When the slide valve is open the said closed part of the closure element and the lateral indentation are situated between a stuffing box and the tube of the sampling column. In the closed position this indentation is situated on the far side of the stuffing box inside an adjoining metal pressure bush, and at the same time the closed part of the closure element is situated in the stuffing box. The tightness of the closure element in the slide valve is achieved by making the stuffing box resilient, using elastic freely slidable material, preferably polytetrafluorethylene.

At the end of the sampling column used for drawing in or introducing the sample and also for the metering of the sample it is advantageous to use a sliding valve whose closure element outside the sliding valve is in the form of a sampling probe, for which purpose the closure element is extended as a capillary probe ending in a closed point and also having, below that point, a lateral indentation which frees the capillary bore. The closure element is guided

in a guide sleeve and is fastened to the latter only at the end formed as a connector.

The method of the invention is advantageously applied with the aid of the apparatus of the invention by sucking into the sampling column from the mixture in gas and/or vapour form an amount (of between 0.01 and 0.5 ml of the material to be sampled) which is suitable for gas chromatography analysis and which can be approximately determined beforehand. For this operation good results have been obtained in particular with proportioning syringes having gastightly movable pistons and applied to the rear closure device of the sampling column, since these syringes enable a corresponding volume of gas of the material being sampled to be sucked into the sampling column. While the sampling probe is still in the gas and/or vapour mixture which is to be analysed, the two closure devices are closed.

During the taking of the sample the temperature of the material to be sampled may be in the range from -100°C to $+250^{\circ}\text{C}$. In order to avoid alterations of the composition of the material sampled, at least the sampling probe and the closure device of the sampling column connected to it must be heated to a temperature of a few degrees above the dew point of the material to be sampled before the sample is taken. During the taking of the sample the material sampled may be under elevated or under moderately reduced pressure.

The residue of sampled material remaining in the capillary tube of the sampling probe is removed in order to exclude any further possibility of alteration of the composition of the sampled material during the subsequent metering of the sample. For this purpose a current of inert gas is blown into the indentation in the sampling probe in order to flush out residues of sampled material from the sampling probe, the closure element, the metallic pressure bush, and the casing surrounding the latter.

For the purpose of metering into an analysis apparatus, particularly a gas chromatography column, the preferably conical connectors of the closure elements are gastightly connected to two capillary inlets of a four-way cock (not shown) of the gas chromatograph used. For this purpose the connectors are expediently pressed into coacting connectors which are in the form of chambered cylindrical bushes of an elastic, freely slidable material, for example polytetrafluoroethylene and which are situated at the end of the capillary inlets. Before the metering of sample the sampling column is, if necessary, heated to a temperature above the dew point of the sample by direct low-voltage heating, the closure devices are opened, and the four-way cock is operated to pass the current of carrier gas into the sampling column. Together with the current of carrier gas the sample passes quantitatively into the gas chromatography column of the

shown that a sample of material taken at 80°C underwent no variation in respect of composition after a storage time of more than 400 hours at room temperature.

- 5 The invention permits the uniform analysis of gas and/or vapour mixtures having a wide boiling range. Thus, in the analysis of sampled material consisting of a mixture of gas and vapour having a dew point above room temperature, the separation of the material into a gas fraction and a liquid fraction, which leads to condensation, is eliminated. This also means the elimination of the irreversible alteration of the gas sample, for example by sorption, and of the liquid sample, for example by degasification, during transport to the analysis apparatus and storage until fed into the latter. Furthermore, this also means the elimination of error in the determination of the quantitative ratio of the gas fraction and liquid fraction, which hitherto gave a false result for the complete analysis. Instead of two separate analyses for the gas fraction and for the liquid fraction, there is now only a single analysis.
- 25 The method of the invention will be explained more fully below with reference to one example of embodiment. The appertaining drawings show, as apparatus according to the invention, the sampling column (Figure 1) and one of the slide valves used as a closure device together with the sampling probe (Figure 2).
- 30 In a reactor having a length of several metres the reaction of a mixture of hydrocarbons is followed by gas chromatography analyses both in respect of its specific course and in respect of its progressive degree of conversion along the reactor. The reaction mixture consists of saturated and unsaturated hydrocarbons and in accordance with its composition has a dew point of 50 to 60°C. Along the entire reaction chamber samples are taken from a number of sampling connections disposed on the reactor. The connector 6 of the sampling column is in the form of a cone and during the taking of a sample is gastightly connected with the aid of a suitable adaptor to a commercially available injection syringe having a displacement volume of 0.5 ml. For the purpose of taking a sample the tip 18 of the sampling probe 4, which tip is closed at its front end, and the lateral indentation 17 of the sampling column, which has been pre-heated to 80°C. in a drying chamber, are pushed, with the slide valves 8 closed, so far through the rubber disc of one of the sampling connections that the indentation 17 of the sampling probe 4 is completely surrounded by the sampled material flowing past. By simultaneous displacement of the guide sleeves 20, as well as of the closure elements 10 connected with the guide sleeves 20 of the slide valves 8 in the direction of the tube 1 as far as the stop surface 9, the sampling column is now opened. The end faces 13 of the closed ends 12 of the closure elements 10 are now located just above the wire fabric screen 7. By pulling

out the piston of the injection syringe gastightly connected to the sampling column, a volume of 0.2 ml, which is convenient for subsequent feeding into the gas chromatography column, is sucked into the indentation 17 of the sampling probe 4, through the common capillary bore 11 of the sampling probe 4 and closure element 10, and by way of the indentation 14 into the sampling column tube 1, which is of stainless steel and has a length of 300 mm with an inside diameter of 2mm. After about one second, pressure equalisation is achieved and the sampling column is closed by movement of the guide sleeves 20 as well as of the closure elements 10 connected with the guide sleeves 20 of the slide valves 8 in the opposite direction, as far as the stop surfaces 19. The closed ends 12 of the closure elements 10 are now located inside the stuffing boxes 15 of the slide valves 8. Only then is the injection syringe taken off the connector 6 and the sampling probe 4 removed from the sampling connection on the reactor. In the same way further samples can be taken at the same time with other sampling columns, if desired.

Before the sampling column is connected to the analysis apparatus, inert gas is blown in through the indentation 17 in order to clean the capillary bore of the sampling probe 4 and of the closure element 10 to remove residues of sampled material, this gas escaping by way of the indentation 14 through the annular gap between the pressure bush 16 and the closure element 10 and through the bore 21 of the casing 22 into the open.

For the purpose of introducing the sample contained in the sampling column into the carrier gas current of a gas chromatography column, the connectors 5, 6 of the closure devices 2, 3 are gastightly pressed into coaxial connectors in the form of chambered cylindrical polytetrafluoroethylene bushes which are provided on the end of two capillary inlets of a four-way cock on the analysis apparatus. The tube 1 of the sampling column is heated to 80°C. by a low voltage of about 1.5 V, and the guide sleeves 20, as well as the closure elements 10 connected with them are moved in the direction of the tube 1 as far as the stop surfaces 9 in order to open the two slide valves 8.

By switching over the four-way cock, carrier gas is passed through the connector 6 into the sampling column and the sample is introduced as a short vapour plug through the indentation 14 and the capillary bore 11 of the closure element 10 and the sampling probe 4, and then through the indentation 17 into the capillary pipe provided on the four-way cock and connected to the connector 5, and thus into the separating column of the gas chromatography apparatus.

The sample can be introduced into the analysis apparatus immediately after the sample has been taken, but also may be introduced thereinto after storage for a long period. Gas

chromatography analyses of two parallel samples of the hydrocarbon reaction mixture, which were made directly after the sample was taken (sample 1) and after storage of the sample in the sampling column for 340 hours (sample 2), gave results showing no important deviation in the composition of the sample; see Table 1. The deviations which occurred are without exception due to the error of the gas chromatography analysis method. The random error of analysis when applying the method of the invention and the apparatus of the invention are shown in Table 2 in the form of the results of three determinations of a hydrocarbon reaction mixture (samples 3, 4, 5). Samples 3, 4, and 5 were taken simultaneously from the material sampled for this examination, in order to exclude any variation of the composition of the material during the taking of the sample.

The abovementioned vapour analyses from sampling columns were effected by gas chromatography analysis utilising a flame ionisation detector followed by a digital integrator and on-line computer processing (results indicated in area per cent).

TABLE 1

Component	Sample 1	Sample 2
1	6.22 %	6.23 %
2	23.69 %	23.83 %
3	15.22 %	15.32 %
4	0.10 %	0.11 %
5	8.58 %	8.67 %
6	0.93 %	0.94 %
7	0.04 %	0.04 %
8	2.12 %	2.12 %
13	42.10 %	41.75 %

TABLE 2

Component	Sample 3	Sample 4	Sample 5
1	0.97 %	0.96 %	0.91 %
2	2.76 %	2.78 %	2.69 %
3	4.85 %	4.91 %	4.86 %
4	0.11 %	0.11 %	0.11 %
5	2.99 %	3.03 %	2.96 %
6	0.42 %	0.42 %	0.42 %
7	0.32 %	0.32 %	0.32 %
8	0.26 %	0.27 %	0.26 %
9	0.99 %	1.01 %	0.99 %

TABLE 2 (continued)

Component	Sample 3	Sample 4	Sample 5
10	0.42 %	0.29 %	0.42 %
11	0.20 %	0.15 %	0.20 %
12	1.15 %	1.12 %	1.13 %
13	1.01 %	1.04 %	1.01 %
14	7.98 %	7.92 %	7.93 %
15	1.31 %	1.32 %	1.31 %
16	0.59 %	0.61 %	0.58 %
17	0.28 %	0.33 %	0.29 %
18	0.05 %	0.06 %	0.06 %
19	0.04 %	0.05 %	0.05 %
20	0.09 %	0.14 %	0.09 %
21	0.04 %	0.06 %	0.05 %
22	0.07 %	0.07 %	0.07 %
23	0.07 %	0.07 %	0.07 %
24	72.83 %	72.80 %	72.99 %
25	< 0.001 %	< 0.001 %	< 0.002 %
26	0.19 %	0.18 %	0.24 %

WHAT WE CLAIM IS:—

1. A method for the discontinuous sampling of gases, vapours or mixtures thereof, at temperatures above their dew point from product flows, reaction chambers, or vessels, and for introducing those samples in the form of gas, vapour or mixtures of gas and vapour into analysis apparatus, more particularly into gas chromatography apparatus, wherein an amount suitable for subsequent analysis - namely a volume of between 0.001 and 5 ml, but preferably between 0.01 and 0.5 ml - of the material in gas and/or vapour form that is to be analysed is drawn in or introduced into a tube which is provided with closure devices at both ends, by a sampling probe, while the sampling probe, the closure devices and the tube - or at least the sampling probe and the tube closure device which is connected thereto - are at a temperature above dew point of the material samples, and while during the drawing-in or introduction of the sampled material into the tube by the sampling probe no fraction of the sampled material shall reach the opposite end of the tube which is dimensioned in length according to the required volume of the sampled material; then the closure devices are closed, the sampling probe is removed from the material being sampled, the sampling column - consisting of the tube, closure devices and sampling probe - is connected either immediately or after its storage to the analysis apparatus, and the sample contained in the sampling column is introduced into the analysis apparatus by way of

a gastight connection with the aid of a gas current after the closure devices have been opened.

2. A method as claimed in Claim 1, wherein the closure devices of the sampling column are opened only after the sampling probe has been introduced into the material of which a sample is to be taken and optionally after the sampling probe has been flushed out with that material.

3. A method as claimed in Claim 1 or 2, wherein for the purpose of drawing in a sample into the sampling column, a volume of gas corresponding to the sampling volume is drawn off from the sampling column by way of the sampling column closure device which is located at the rear end of the sampling column in relation to the direction in which the sampled material flows in.

4. A method as claimed in Claim 1, 2 or 3, wherein before the sampling column is connected to the analysis apparatus, residues of sampled material are flushed out of the sampling probe.

5. A method as claimed in any one of Claims 1 to 4, wherein the sample contained in the sampling column is flushed out of the sampling column into the analysis apparatus in a direction opposite to that in which it flows in during the taking of the sample.

6. A method as claimed in any one of Claims 1 to 5, wherein immediately before and during introduction into the analysis the sample is heated to a temperature above its dew point.

7. A method as claimed in any one of Claims 1 to 6, wherein for the purpose of heating the sample, a low voltage is applied to the sampling column.

8. An apparatus for the discontinuous sampling of gases, vapours or mixtures thereof, at temperatures above their dew point from product flows, reaction chambers or vessels, and for introducing the samples in the form of gas, vapour or mixtures thereof, into analysis apparatus, more particularly into gas chromatography apparatus, for performing the method according to any one of Claims 1 to 7, comprising a sampling column consisting of a tube which has an inside diameter of between 0.1 and 10 mm, preferably between 0.2 and 6 mm, and a length conforming with the required volume of the sampled material - namely a tube length which is generally such that the free internal volume of the tube is from 2 to 5 times as great as the sample volume to be metered into analysis apparatus to ensure that when an amount of sampled material suitable for subsequent analysis is drawn in no part of it will reach the rear end of the tube of the sampling column - and which has at each end a gastight closing closure device having no dead spaces and at one end is provided with a sampling probe, connectors being provided on both closure devices for gastight connection.

9. An apparatus as claimed in Claim 8, wherein the tube of the sampling column contains a sorption agent.

10. An apparatus as claimed in Claim 8, wherein the tube of the sampling column is filled with a granular material which is retained at both ends of the tube by wire fabric screens.

11. An apparatus as claimed in Claims 8, 9 or 10, wherein the tube of the sampling column forms the heating resistor of a low-voltage heating system.

12. An apparatus as claimed in any one of Claims 8 to 11, wherein the closure devices provided at each end of the tube of the sampling column comprise in each case a slide valve whose closure element consists of a tube having a capillary bore, the capillary bore at the end directed towards the tube being closed from the end face right up to the indentation, its closure element being displaceable in its longitudinal direction between two stop surfaces in such a manner that when the slide valve is open the indentation is situated between the stuffing box and the tube and that when the slide valve is closed the indentation is situated entirely inside the pressure bush and the end closure from the end face to the indentation is situated in the stuffing box.

13. An apparatus as claimed in Claim 12, wherein the closure element in the slide valve is sealed by a resiliently chambered stuffing box of elastic, freely slidable material.

14. An apparatus according to Claim 13, wherein the resiliently chambered stuffing box in the slide valve is made of polytetrafluoroethylene.

15. An apparatus as claimed in any one of Claims 12 to 14, wherein the closure element is formed outside the slide valve as the sampling probe, the probe itself ending into a closed point at the front and freeing at the indentation the common capillary bore of the closure element and of the sampling probe.

16. An apparatus as claimed in any one of Claims 8 to 15, wherein the closure element is guided in a guide sleeve, one end of the guide sleeve being in the form of a connector, preferably conical, only the said one end being fastened to the closure element.

17. A method of discontinuous sampling of gases, vapours or mixtures thereof as claimed in Claim 1 and substantially as hereinbefore described.

18. An apparatus for the discontinuous sampling of gases, vapours or mixtures thereof substantially as herein described with reference to and as shown in the accompanying drawings.

VENNER, SHIPLEY & CO.,
Chartered Patent Agents,
Rugby Chambers,
2, Rugby Street,
London, WC1N 3QU.
Agents for the Applicants.

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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
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Sheet 1*

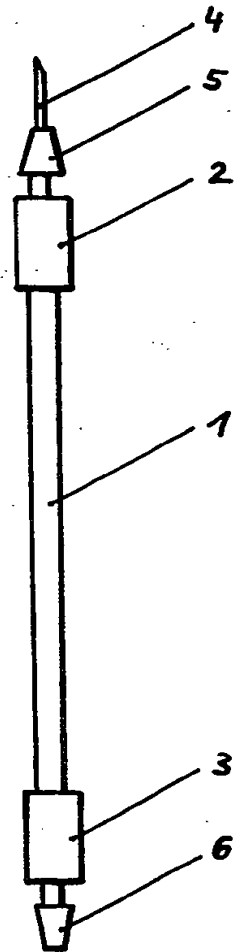


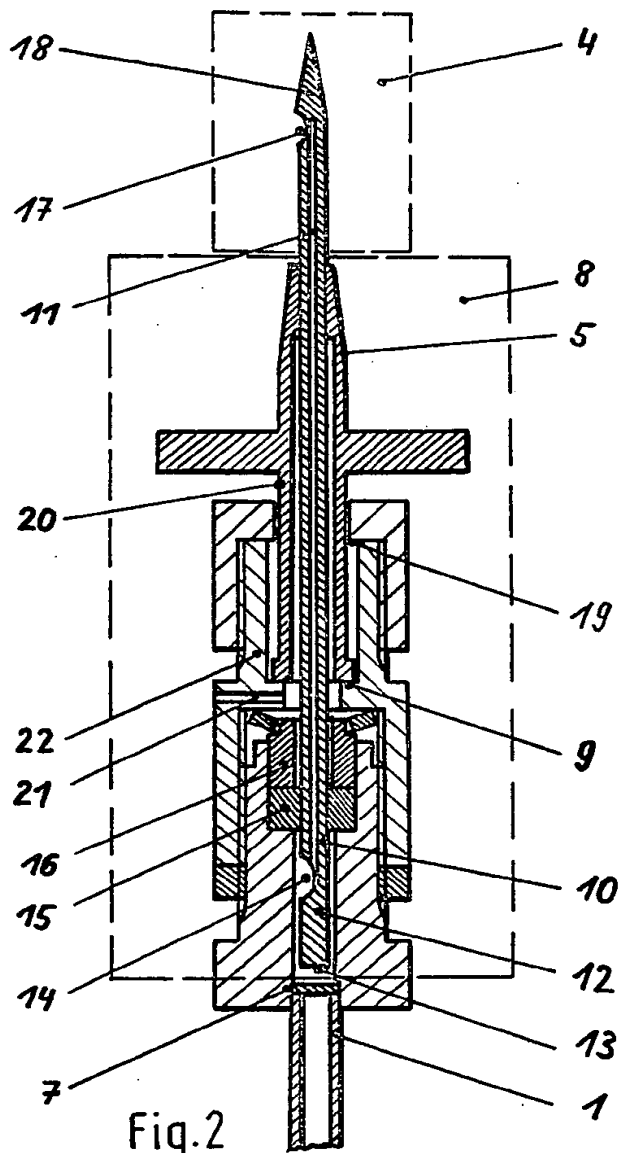
Fig. 1

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COMPLETE SPECIFICATION

2 SHEETS

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Sheet 2*



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